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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 673 892 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 95103139.2

(22) Date of filing: 06.03.95

(51) Int. Cl.6: C03C 3/097, C03C 3/105, C03C 21/00, H01S 3/17

(30) Priority: 25.03.94 US 217734

(43) Date of publication of application: 27.09.95 Bulletin 95/39

(84) Designated Contracting States: DE FR GB IT NL

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(54) Optical signal amplifier glasses.

(57) An optical signal amplifier comprising an optical waveguide fiber integrated by thallium ion exchange in a boron-free silicate glass doped with up to 5 weight % erbium oxide, the glass having a base composition, as calculated in weight percent on an oxide basis, consisting essentially of

SiO_2	38-67	Al_2O_3	1.5-4.5
Na_2O	0-20	ZnO	1.5-8
K_2O	0-25	Li_2O	0-1
Na_2O+K_2O	15-30	PbO	0-37
BaO	0-7	P_2O_5	0-10
		P_2O_5+PbO	5-37

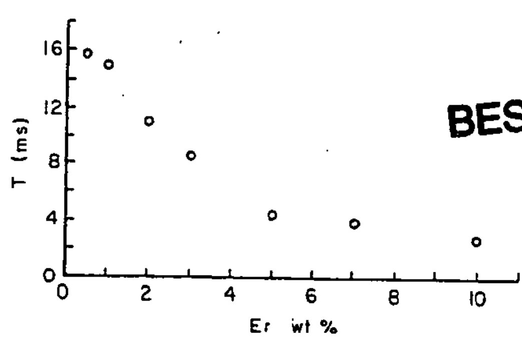

Fig. 1

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SiO_2	38-67	Al_2O_3	1.5-4.5
Na_2O	0-20	ZnO	1.5-8
K_2O	0-25	Li_2O	0-1
$Na_2O + K_2O$	15-30	PbO	0-37
BaO	0-7	P_2O_5	0-10
		$P_2O_5 + PbO$	5-37

BRIEF DESCRIPTION OF THE DRAWING

FIGURES 1 and 2 in the accompanying drawing are graphical representations of relevant properties measured on glasses in accordance with the present invention.

DESCRIPTION OF THE INVENTION

The present invention provides a family of glasses having general utility, particularly in lighting, optical and electronic applications. However, the glasses have unique features that render them of particular value in the production of an integrated, optical waveguide signal amplifier.

One feature of the present glasses is their freedom from boric oxide (B_2O_3). As explained earlier, it has been known that B_2O_3 exerts a very strong degrading effect on the spectroscopic effects in a glass doped with a rare earth metal oxide. However, B_2O_3 is commonly used for its beneficial effects on coefficient of thermal expansion and temperature-viscosity relationship in silicate glasses. The constituents of the present glasses are so proportioned that B_2O_3 is unnecessary and is omitted.

A further feature of the present glasses is their ability to be doped with relatively large amounts of erbium oxide (Er_2O_3). In the absence of B_2O_3 in the base glass, such doping has been found to provide excellent fluorescent effects which are vital for signal amplification by laser light pumping. In particular, the present erbium-doped, boron-free glasses may have an excited-state lifetime that is at least 8 ms in length. The emission bandwidth of the 4 I 13/2-4 I 15/2 transition is around 20 nm, and the emission cross-section at a wavelength of 1538 nm may be higher than 5×10^{-25} m^2.

The glasses of the invention are predicated in large measure on my discovery that the B_2O_3 content in prior borosilicate glasses can be replaced with oxides of lead (PbO) and/or phosphorus (P_2O_5). When such replacement is made, the depressing effect of B_2O_3 is avoided, and the desirable properties of an erbium-doped glass are obtained. Furthermore, the new B_2O_3-free glasses possess essentially as good properties for thallium ion exchange as did the prior borosilicate glasses. This enables burying an optical waveguide in the glass by ion exchange.

The properties required for thallium ion exchange are:

1. A transformation range (Tg) below 500°C to permit thallium ion exchange in the temperature range of 350-450°C.
2. A sufficient amount of Na and/or K ions to exchange with thallium.
3. A ratio of K/Na ions equal to or greater than 2 to preserve the rate of exchange with thallium.
4. Good durability of the glass to withstand chemical attack during the masking and ion exchange processes.

My new glasses are capable of meeting these requirements, as well as providing the emission characteristics necessary for successful signal amplification. The glasses have a silica base, are boron-free, and must contain at least one oxide selected from Na_2O and K_2O, and at least one oxide selected from P_2O_5 and PbO. Optionally, the glasses may contain minor amounts of divalent oxides, particularly BaO and ZnO.

Alumina (Al_2O_3) is effective in broadening the erbium emission spectra at around 1.5 microns. Therefore, the glass must have an Al_2O_3 content sufficiently high to achieve this effect. Al_2O_3 also tends to improve glass durability, and thereby enable the glass to withstand chemical attack during processing. However, the Al_2O_3 content must not exceed about 4.5% to avoid a glass transformation range higher than 500°C.

The alkali metal oxides, Na_2O and K_2O must be present to provide a glass that is ion-exchangeable with thallium ions. The oxides also serve to soften the glass, that is provide a low Tg glass. Preferably, the glasses contain both oxides with a K_2O:Na_2O ratio of at least 2:1. A ratio greater than 2:1 appears to provide optimum conditions for ion exchange with thallium. While either alkali metal oxide may be omitted from the present glasses, their total content must be within the range of 15-30 weight %. The maximum

TABLE III

Compositions and Their Properties

Wt %	1	2	3	4	5	6	7
SiO_2	67	54.7	55.8	55.4	38.3	55.8	54.2
Na_2O	6.4	5.7	5.7	5.8	4.7	5.7	0
K_2O	19.1	17.1	17.1	17.3	14	17	24.9
BaO	3.2	2.8	2.8	0	2.3	2.9	2.8
Al_2O_3	2.1	1.9	1.9	1.9	1.5	1.9	1.8
ZnO	2.2	1.9	1.9	3.4	1.5	1.9	1.9
Li_2O	0	0.9	0	1	0.8	0	0
PbO	0	15	14.8	15.2	36.9	14.8	14.4
P_2O_5 excess	5	0	5	0	0	5	5
Properties							
Tg(°C)	435	416	412	416	377	405	435
nd	1.504	1.544	1.542	1.544	1.613	1.5391	1.5373
T(ms)	9.8	9	9.8	8.5	12	10	>11
Er^{3+}(cm^3) 10E-20	1.58	1.76	1.18	1.74	1.43	0.59	0.6
Emission Bandwidth (nm)	21	21	21	21	20	20	20
Emission Peak(nm)	1538	1538	1538	1538	1538	1537	1537

FIGURE 2 is a plot showing the emission cross-section and the absorption cross-section for a silicate glass having an erbium doping level of 3.3×10^{19} atoms/cm^3 and a lifetime of about 8 ms. Wavelength is plotted in nanometers (nm) on the horizontal axis, while cross-section in meters^2 $\times 10^{-25}$ is plotted on the vertical axis. Based on these plots, a gain of 0.5 dB has been determined for a length of about 4 cm.

An optical waveguide for present purposes begins with melting a glass having a composition as defined above. A thin wafer or flat disk is formed from the melt. This may be a pressed body, or one cut from a larger body. In either case, the body is finished as required.

The glass body is then selectively coated with a mask preparatory to treatment in a molten salt bath. The selective coating is impervious to ion migration. It covers the glass surface, except for a narrow zone left exposed on the glass surface. The mask may be an oxide coating as described in United States Patent No. 3,857,689 (Koizumi et al.), or may be any other suitable resist coating.

The masked glass body is then exposed to a thallium salt bath to exchange thallium ions for sodium and/or potassium ions from the glass. The salt bath is at a temperature in the range of 350-450 °C and exposure will be for a time sufficient to form a fibre-like, ion-exchanged zone in the exposed glass surface. The masked glass body is then exposed to an alkali metal salt bath, e.g. a KNO_3 bath, at the same temperature, to drive the thallium-ion fibre into the glass by further ion exchange. The protective mask is then removed to complete the process.

Claims

1. A glass having ion exchange properties particularly adapted to production of optical signal amplifiers operating at a wavelength of about 1.5 microns, that is free of B_2O_3, that is capable of being doped with up to 5 weight % erbium oxide, that has good spectroscopic properties and that has a base glass composition consisting essentially of, on an oxide basis as calculated in weight percent,

SiO_2	38-67	Al_2O_3	1.5-4.5
Na_2O	0-20	ZnO	1.5-8
K_2O	0-25	Li_2O	0-1
$Na_2O + K_2O$	15-30	PbO	0-37
BaO	0-7	P_2O_5	0-5
		P_2O_5 + PbO	5-37

2. Glass in accordance with claim 1 having a base composition consisting essentially of, on an oxide basis as calculated in weight percent

SiO_2	52-56	ZnO	1.5-8
K_2O	0 - 25	Li_2O	0 - 1
Na_2O	0-20	PbO	10-15
$Na_2O + K_2O$	18 - 26	P_2O_5 excess	0 - 5
$K_2O:Na_2O$	2-3.3:1	P_2O_5 + PbO	15 - 20
BaO	0 - 3		
Al_2O_3	1.5 - 4.5		

3. Glass in accordance with claims 1 or 2 having a transformation temperature below 500 °C whereby thallium ion exchange can occur at a temperature in the range of 350-450 °C.

4. Glass in accordance with claims 1, 2 or 3 wherein the composition contains both K_2O and Na_2O, the total of these oxides being 15-30% by weight.

5. Glass in accordance with claim 4 wherein the $K_2O:Na_2O$ ratio is at least 2:1.

6. Glass in accordance with any one of claims 1-5, wherein the glass composition is modified within a selective area by at least partial replacement of potassium and/or sodium ions by thallium ions.

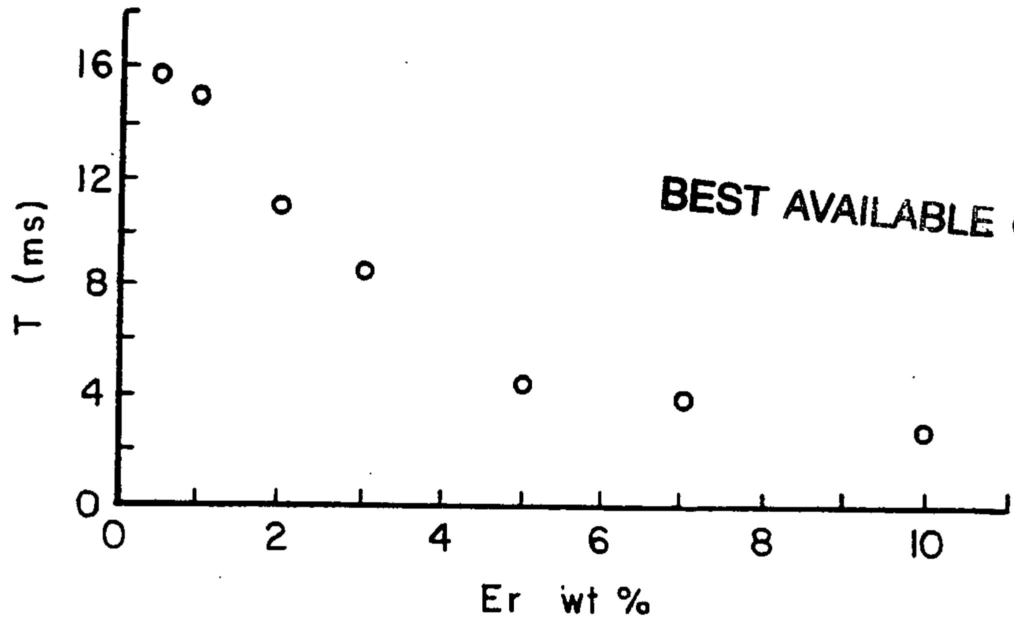
T (ms)
16
12
8
4
0
0
2
4
6
8
10
Er wt %

Fig. 1

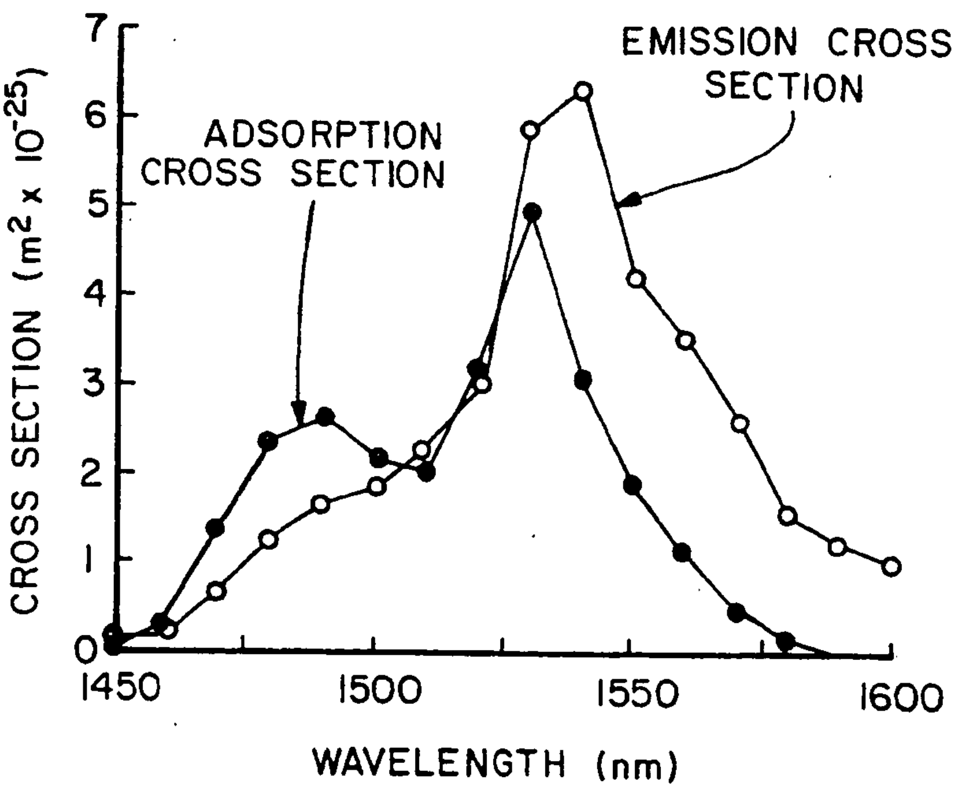
CROSS SECTION ($m^2 \times 10^{-25}$)
7
6
5
4
3
2
1
0
1450
1500
1550
1600
WAVELENGTH (nm)
EMISSION CROSS SECTION
ADSORPTION CROSS SECTION

Fig. 2